Atty docket no: 52309-P004US
Client ref: ARB/P1846US00

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

Ward, Luke

Application no: 10/516,448

PCT filed: May 30, 2003

Title: Application of a coating forming material onto at least one substrate

Examiner: Burkhart, Elizabeth A

Art unit: 1715

Confirmation no: 4683

DECLARATION UNDER 37 C.F.R. 1.132

DECLARATION OF PROFESSOR JAS PAL SINGH BADYAL

1. I, Professor Jas Pal Singh Badyal, am a Full Professor of Chemistry at Durham University, England. My curriculum vitae, showing my qualifications and relevant technical experience, is annexed to this declaration as Annex I.

2. I have read the above-referenced patent application ("the present application") and its currently pending claims. I have also read the Office Action dated October 7, 2010, and both WO-02/28548 (Goodwin et al) and WO-98/58117 (Badyal et al), which are cited in that Office Action. I was the primary named inventor on both the Goodwin et al and the Badyal et al patent applications.

3. I have been asked to comment on the technology described in Goodwin et al and Badyal et al; on the way in which a person of ordinary skill in the art would interpret the two documents; and on the likelihood of that person combining the teachings of the two documents. I believe that I am competent to do this, given that: (i) I was the primary named inventor on both documents; (ii) I was the only named inventor on either document who had any prior expertise of either "pulsed gas-phase" plasma deposition or plasma deposition using atomised liquid droplets at

atmospheric pressure; (iii) all of the plasma deposition work described in both Goodwin et al and Badyal et al was carried out under my direct supervision in my research laboratory at Durham University by PhD students Luke Ward and Stephen Coulson respectively; and (iv) studies relating to the pulsed gas-phase technology of Badyal et al had been ongoing in my laboratory from 1992 to 1995, and studies relating to the Goodwin et al system, using atomised liquid droplets at atmospheric pressure, had been ongoing in my laboratory between 1995 and 1998.

4. Goodwin et al relates to a liquid-phase coating system in which the coating material is introduced in the form of atomised liquid droplets, at atmospheric pressure. Thus in this system, the coating material is not in gaseous form even though the surrounding exciting medium may be. Badyal et al, in contrast, relates to an entirely gas-phase deposition system carried out at reduced pressures. I believe that at the priority date of the present application (June 1, 2002), a person of ordinary skill in the art would have been discouraged from combining the two types of technology.

5. Gas-phase and liquid-phase plasma deposition systems are not analogous. This means that the skilled person would not have expected it to be straightforward to combine the teachings of Goodwin et al and Badyal et al. This is consistent with the fact that Goodwin et al, in proposing the use of atomisation in a plasma deposition system, made no mention of the possibility of pulsing the exciting medium. The document discussed earlier plasma deposition processes only from the point of view of their disadvantages (the requirement for reduced pressure, and the resultant expense – see paragraph [0003]; the inability to work directly with liquid or solid coating materials – see paragraph [0014]; and the potential loss of chemical properties in the deposited coating – see paragraph [0018]). Despite the fact that pulsing was already well known in gaseous systems, my fellow inventors Goodwin et al and I did not think that it would be obvious or straightforward to adopt that technique in our own system, hence our failure to refer to pulsing in the document. Nor therefore did we provide any incentive for the reader to return to the art on gas-phase plasma deposition in order to improve upon our system.

6. I believe this is because the physical chemistry involved in a gas-phase plasma deposition process is very different to that which governs a process such as the one disclosed in Goodwin et al, where a liquid coating forming material is atomised into the exciting medium. So too are the mechanisms which act on the various fluids present, and which govern the excitation and eventual deposition of the coating materials. On this basis, the person of ordinary skill in the art

would not with confidence expect the advantages of pulsing in gaseous systems to transfer readily to systems involving atomised liquids.

7. The general principle behind the use of pulsing in gas-phase systems is that during the limited "on" period the plasma can excite the molecules of the coating forming material sufficiently to allow them to react with one another, but not enough to cause widespread fragmentation. During the "off" period the excited molecules react to form the intended coating. In this way, pulsing can help to maintain the structural integrity of the coating. It would not, however, have been clear to the skilled person whether or how those mechanisms would apply to atomised *droplets* of coating forming material. In a purely gaseous system, all molecules, ions and radicals are free to move around. In the atomised system this is not the case: there are constraints at the macromolecular (droplet) level, for example due to surface tension and molecular cohesion, and there are the effects of liquid evaporation to take into account. In a liquid-phase system, the substrate surface can become wetted by the atomised coating material; in the gas-phase process of Badyal et al, in contrast, there are no droplets present to spread across the substrate.

8. Moreover, in an atomised liquid system such as that shown in Goodwin et al, molecules can become trapped within the droplet structure, thus preventing them from behaving in the way that they would if present as a gas. Unexcited molecules (the precursors to the coating species) can become trapped within the droplets, and deposited into the coating layer before having the chance to react. The exciting medium begins to polymerise and cross-link the liquid droplets rapidly following atomisation, an effect which works from the outside of each droplet towards its centre. This tends to form a "skin" of reacted molecules: inside the skin, unreacted or partially reacted molecules remain trapped. Such complications do not arise in purely gaseous systems.

9. Any polymerisation process generates, in addition to the desired polymer, a distribution of oligomers of varying molecular weights. Lower molecular weight oligomers which become trapped in the droplets will compromise the structural integrity – and hence the properties and performance – of the coating. These species can also leach out during subsequent use of the coated product, causing toxicity issues.

10. The process of Goodwin et al is carried out at atmospheric pressure: the document is clear that this is an essential, and advantageous, feature of the process described. However this can exacerbate the entrapment problem. Under vacuum, lower molecular weight impurities can more readily be removed, but at atmospheric pressure they are more likely to remain

trapped both within the atomised droplets and subsequently in the deposited coating layer. When operating the process described in Goodwin et al, we generally noted a strong smell afterwards and subjected the coated products to vacuum treatment following deposition, to remove labile materials trapped inside the coatings (see Example 1 of Goodwin et al, and paragraph [0024]).

11. I believe that the person of ordinary skill in the art, having recognised the entrapment problem in the system of Goodwin et al, would have had no reason to believe that pulsing would solve it. Rather, he would have expected pulsing to increase the problem, in that the "off" periods, and the consequent lower average energy of the exciting medium, would increase the risk that molecules in the droplet centres would be unable to react in the desired manner. This too would have discouraged him from combining Goodwin et al with Badyal et al. His most obvious solution to the entrapment problem would probably have been to *increase* the overall power of the excitation field: he would have expected this to allow greater droplet penetration, and thus to avoid the formation of a reacted "skin" surrounding an unreacted centre. Yet increasing the power could also have been expected to reduce the structural integrity of the coating, due to increased fragmentation of the coating forming material.

12. Moreover, the entrapment problem which arises with the system of Goodwin et al is also well documented for systems where *gaseous* precursors are used in combination with pulsed plasmas at atmospheric pressure. See for example Annex II, which is a paper by Donohoe and Wydeven, *ISPC 4 International Symposium in Plasma Chemistry* No 4 (1979): 765-771. This paper describes atmospheric pressure pulsed discharge polymerisation of ethylene (see the abstract and introduction on page 765). In the third paragraph of the results section (page 766), the authors refer to an olefinic odour (similar to ethylene) in the polymerised films, showing that unreacted material had become trapped within the films during their formation. Since the combination of Goodwin et al with Badyal et al would also result in an atmospheric pressure, pulsed system, the skilled person would expect it to suffer from similar entrapment issues, exacerbated by the use of atomised droplets. He would therefore be further discouraged from attempting the combination.

13. Badyal et al does not address the entrapment problem because the problem does not occur when the coating precursors are free within a low pressure gas phase system rather than trapped within liquid droplets and constrained by atmospheric pressures. Thus, the skilled person would again be concerned that by combining Badyal et al with Goodwin et al, he would induce complications which are simply not foreseen, much less addressed, in Badyal et al. This

underlines the fundamental differences between a liquid-phase and a gas-phase system, and thus reinforces my belief that the person of ordinary skill in the art would have been discouraged from combining the systems of Goodwin et al and Badyal et al.

14. At the time that Goodwin et al was published, on April 11, 2002, it represented a departure from the widely known and well understood gas-phase technology. It was not, at that stage, so obvious that techniques used in gas-phase technology would work in the same way in the new atomised liquid system: rather, I believe that the skilled person would quite reasonably have expected complications had he tried to transfer the teachings from the known field across into the new one. It is telling that Goodwin et al itself says nothing about the application of a pulsed exciting medium to the atomised system it proposes.

15. Therefore, I conclude that the person of ordinary skill in the art would have been discouraged from combining the teachings of Goodwin et al and Badyal et al, at the priority date of the present application.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardise the validity of the application or any patent issued thereon.

Declarant's signature:

Jas Pal Badyal

Jas Pal Singh BADYAL

16th January 2011

Date

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DECLARATION UNDER 37 C.F.R. 1.132 (ANNEX I)

DECLARATION OF PROFESSOR JAS PAL SINGH BADYAL

ANNEX I

This is Annex I referred to in my declaration.

Declarant's signature:

Jas Pal Singh BADYAL

16th January 2011

Date

CURRICULUM VITAE: JAS PAL BADYAL

1 Date and Place of Birth

20th March 1964, Wolverhampton, England. Age = 46 years.

2 Academic Qualifications

B.A./M.A.:	in *Natural Sciences*, Cambridge University	June 1985
Ph.D.:	*Surface Science Related to Heterogeneous Catalysis: Structure, Chemistry and Catalysis at the Ruthenium-Titania Interface*, with Professor Richard Lambert at the Department of Chemistry, Cambridge University	June 1988

3 Academic Employment

- Junior Research Fellow, King's College, Cambridge University — Feb 1988 - Oct 1989
- Oppenheimer Fellow, Cambridge University — Oct 1988 - Oct 1989
- Lecturer, Department of Chemistry, Durham University — Oct 1989 - March 1996
- Professor, Department of Chemistry, Durham University — April 1996 – Present

4 Academic Awards / Prizes

- *1993 Harrison Prize for Most Meritorious and Promising Original Investigations in Physical/Theoretical Chemistry*, the Royal Society of Chemistry — March 1994
- *1995 Burch Prize for Outstanding Work in the Field of Surface Science*, The British Vacuum Council (this is administered jointly by the Institute of Physics and the Royal Society of Chemistry). — Nov 1994
- *$15,000 DuPont Award in Recognition of Fundamental Studies Related to Plasma Chemistry.* — July 1997
- Winner of *1999 Procter & Gamble International UERP competition, $100,000* — April 1999
- *EPSRC Advanced Research Fellowship* for 5 years — Oct 2000

5 International Journal Editorial Board Membership

- Journal of Adhesion Science and Technology — Jan 1996 - Dec 2001
- Plasmas and Polymers — April 1999 – Jan 2005
- Plasma Chemistry and Plasma Processing — May 2005 – present
- ACS Applied Materials & Interfaces — Jan 2011 - present

6 INTERNATIONAL / NATIONAL COMMITTEE MEMBERSHIP

• UK representative on the *Plasma Science and Techniques Division of the International Union for Vacuum Science, Technique, and Applications (IUVSTA)*	April 1998- March 2004
• Co-opted member of British Vacuum Council	April 1998- March 2004
• *International Bunsen Discussion Meeting: Conduction and Transport Mechanisms in Organic Materials: Preparation, Characterization and Applications* Heidelberg, Germany (Joint meeting organized by the Deutsche Bunsen-Gesellschaft, Divisione di Chimica Fisica della Societa Chimica Italiana, Division de Chimie Physique de la Societe Francaise de Chimie, Faraday Division of the Royal Society of Chemistry, and Fachverband Chemische Physik de Deutschen Physikalischen Gesellschaft.)	27-30 Sept 1998
• The Standing Committee on Conferences of the Faraday Division of the Royal Society of Chemistry	Sept 2000- Aug 2003
• International Scientific Committee for 14th International Colloquium on Plasma Processes (CIP'2003), Antibes – Juan-les-Pins, France.	June 29th – 3rd July 2003
• Royal Society Industry Fellowships Scheme Joint Panel	1 Jan 2006 - 31 Dec 2008
• UK representative on international steering committee of n-ABLE (Nanotechnology in Manufacturing)	1st Nov 2005 -
• Chair and organizer of Zing Trends in Surface Chemistry International Conference, Antigua,	7th-10th Jan 2008
• International Scientific Committee for *The 3rd International School of Advanced Plasma Technology*, Villa Monastero, Varenna , Italy.	July 28-July 31, 2008

7 Invitations to Lecture at Overseas International Conferences

- *Plasma Versus Corona Activation of Polymer Surfaces* — 4 Nov 1993
  (Invited Speaker)
  IBM International Symposium on Polymer Surface Modification,
  Las Vegas, USA.

- *Plasma Polymerization of Organosilicon Precursors* — 9 Nov 1993
  (Invited Speaker)
  IBM International Symposium on Plasma Polymerization/Deposition
  Las Vegas, USA.

- *Structure, Chemistry, and Gas Barrier at the AlO_X/PET Interface* — 16-20 Oct 1995
  (Invited Speaker)
  1st International Congress on Adhesion Science & Technology,
  Amsterdam, The Netherlands.

- *Surface Fluorination Versus Oxidation of Polymer Surfaces* — 16-20 Oct 1995
  (Invited Speaker)
  1st International Congress on Adhesion Science & Technology,
  Amsterdam, The Netherlands.

- *XPS Characterization of Polymer Surfaces (Invited)* — 31 Oct 1995
  Danish Society for Polymer Technology
  Copenhagen
  Denmark

- *Structure, Chemistry, and Gas Barrier at the AlO_X-Polymer Interface* — 7-8 May 1996
  (Invited Speaker)
  Pharmaceutical and Medical Packaging '96,
  Copenhagen, Denmark.

- *Plasma Processing of Polymer Surfaces* — 9-13 Sept 1996
  (Plenary Lecture)
  5th International Conference on Plasma Surface Engineering
  Garmisch-Partenkirchen, Germany.

- *Characterization of Polymer Surfaces (Invited)* — 2 Oct 1996
  Danish Society for Polymer Technology
  Copenhagen, Denmark

- *Molecular Reaction Pathways During Plasma Modification of Polymer Surfaces* — 13-17 April 1997
  (Invited Speaker)
  Americal Chemical Society
  Polymer Division Symposium: Plasmas and Polymers
  San Francisco, USA

- *Ultraselective Plasmachemical Reaction Pathways at Solid Surfaces* — 30 Nov - 1 Dec 1998
  (Invited Speaker)
  Materials Research Society Fall 98 Meeting
  Boston, USA.

- *Pulsed Plasma Surface Functionalization* — 15^{th}-20^{th} April 2000
  (Invited Speaker)
  Society of Vacuum Coaters 43rd Annual Technical Conference
  Denver, Colorado, USA

- *Controlled plasmachemical functionalization and adhesion of solid surfaces* — Dec 9-13, 2000
  Poly Millennial 2000

Division of Polymer Chemistry of the American Chemical Society
Macromolecular Plasma Chemistry Symposium
Hilton Waikoloa Villages,
Hawaii

- *Controlled Plasmachemical Functionalization of solid surfaces* — 10-14th June 2001
  (Opening Keynote Lecture)
  CIP'2001 (13th International Colloquium on Plasma Processes)
  Antibes, France

- *Plasma Deposition of Superhydrophobic Surfaces (Invited Speaker)* — Dec 3 - 7, 2001
  7th Pacific Polymer Conference
  Division of Polymer Chemistry of the American Chemical Society
  Macromolecular Plasma Chemistry Symposium
  Oaxaca, México

- *Surface Functionalization and Industrial Applications (Plenary Speaker)* — 18th-19th May 2005
  International Symposium: Plasma Technologies for Industrial applications
  (Textile, Health, Food and Environment)
  Milan, Italy

- *High Throughput Functional Nanocoatings (Invited Speaker)* — 26-28 Sept 2005
  n-ABLE 2005, Nanotechnology in Manufacturing,
  Saarbrucken, Germany.

- *High Throughput Functional Nanocoatings (Invited Speaker)* — 8th-10th Nov 2005
  NanoSolutions 2005
  EXPO XXI, Cologne International Expocentre, Germany

- *High Throughput Functional Nanocoatings (Invited Speaker)* — 17th-18th Nov 2005
  Technical Textiles
  Ghent, Belgium

- *'Re-Usable And Non-Leaching Antibacterial Nanocoatings'* — June 27 - 28, 2007
  (Invited Speaker)
  Antimicrobials in Textiles and Plastics Applications
  IntertechPira, USA
  Prague, Czech Republic

- *Controlled Plasmachemical Functionalization of Solid Surfaces for* — April 28-30, 2008
  Adhesion and Liquid Repellency (Plenary Speaker)
  American Chemical Society 173rd International Rubber Division Technical
  Meeting,
  Dearborn, Michigan, USA

- *Rewritable Bioarrays (Invited Speaker)* — 28-31July 2008
  The 3rd International School of Advanced Plasma Technology,
  Villa Monastero, Varenna , Italy.

- *Bioactive Surfaces (Invited Speaker)* — 15th-19th Sept 2008
  E-MRS (European Materials Research Society)
  Warsaw, Poland

- *Functional Nanocoatings (Invited Speaker)* — 10th-12th March 2009
  Smart Fabrics 2009
  IntertechPira, USA
  Rome, Italy

- *Functional Nanocoatings (Invited Speaker)* — 5-7 July 2010
  International Conference on Plasma Processes and Applications

Kirchberg, Luxembourg

- *Plasmachemical Tailoring of Solid Surfaces (Invited Speaker)* 22-26 August 2010
  240th American Chemical Society (ACS) National Meeting
  Division of Colloid and Surface Chemistry
  Boston, USA

- *Plasmachemical Functionalization of Polymer Surfaces for Adhesion and Liquid Repellency (Invited Speaker)* 22-26 August 2010
  240th American Chemical Society (ACS) National Meeting
  Division of Colloid and Surface Chemistry
  Boston, USA

- *Plasmachemical Deposition of Smart Functionalities (Invited Speaker)* 5-6 Oct 2010
  Food Packaging Innovations
  Graz, Austria

- *Multi-Functional Nanocoatings (Plenary Speaker)* 7-11 Feb 2011
  5th International Conference on Advanced Materials and Nanotechnology (AMN-5)
  Wellington, New Zealand

- *Multi-Functional Nanocoatings* (Invited *Speaker)* 20-22 June 2011
  8th International Conference on Polymer Surface Modification
  Danbury, Connecticut, USA

- *Multi-Functional Nanocoatings* (Invited *Speaker)* 27-29 June 2011
  5th International Conference on Developments in Materials, Processes and Applications of Emerging Technologies
  Alvor, Portugal

8 List of Publications and Patents

8.1 Refereed Journal Papers

J P S Badyal is the principal author unless otherwise indicated by a † symbol. The 20 most significant papers are highlighted in ***bold.***

1) *†The origin of certain features in the Auger spectrum of Ru(0001): Impurities, Auger transitions or diffraction effects?*
J.P.S. Badyal, A.J. Gellman and R.M. Lambert
Surface Science 188 (1987) 557-562.

2) *†Single crystal modelling of the SMSI phenomenon: Structure, composition, electronic effects and CO chemisorption at the Ru(0001)/TiO_x interface*
J.P.S. Badyal, A.J. Gellman, R.W. Judd and R.M. Lambert
Catalysis Letters 1 (1988) 41-50.

3) *†Model studies of the SMSI phenomenon 1.CO and hydrogen chemistry at the Ru-Ti interface*
J.P.S. Badyal, A.J. Gellman and R.M. Lambert
J. Catalysis 111 (1988) 383-396.

4) *†Model Studies of the SMSI Phenomenon at the TiO_x/Ru(0001) Interface*
J.P.S. Badyal, A.J. Gellman, R.W. Judd and R.M. Lambert
Studies in Surface Science and Catalysis: Volume 48: Structure and Reactivity of Surfaces 19-30 (1989, Elsevier, Amsterdam).

5) *†Chemistry and Catalysis at the Metal / Metal Oxide Interface*
J.P.S. Badyal, R.M. Nix and R.M. Lambert
Faraday Discussions Chem. Soc. 87 (1989) 121-132.

6) *†Molecular Mechanism Of Heterogeneous Alkene Epoxidation: A Model Study with Styrene on Ag(111)*
S. Hawker, C. Mukoid, J.P.S. Badyal and R.M. Lambert
Surface Science 219 (1989) L615-L622.

7) *†The Mechanism of Alkene Epoxidation and Epoxide conversion on Single Crystal Silver Surfaces*
S. Hawker, C. Mukoid, J.P.S. Badyal and R.M. Lambert
Studies in Surface Science and Catalysis: New Developments in Selective Oxidation (Elsevier, 1990) 739-746.

8) *†Molecular Mechanism Of Alkene Epoxidation: A Model Study with 3,3-Dimethyl-1-Butene on Ag(111)*
C. Mukoid, S. Hawker, J.P.S. Badyal and R.M. Lambert
Catalysis Letters 4 (1990) 57-62.

9) *†A Model Oxide Catalyst System for the Activation of Methane: Lithium-Doped NiO on Ni(111)*
J.P.S. Badyal, X. Zhang and R.M. Lambert
Surface Science Letters 225 (1990) L15-L19.

10) *†X-ray Photoelectron Spectroscopic Characterization of Oxygen Surface Species on a Doubly Promoted Manganese Oxide Model Planar Catalyst: Significance for CH_4 Coupling*
G.D. Moggridge, J.P.S. Badyal and R.M. Lambert.
Journal of Physical Chemistry 94 (1990) 508-510.

11) *†Novel Photoinduced Surface Oxidation of an Amorphous Semiconductor: An XPS Study of Vitreous Arsenic Sulphide*
A.V. Kolobov, J.P.S. Badyal and R.M. Lambert
Surface Science 222 (1989) L819-L824.

12) *[†]Electroactive Langmuir-Blodgett Films of O-Hexadecylthiocarboxytetrathiafulvalene (HDTTTF)*
A.S. Dhindsa, J.P.S. Badyal, M.R. Bryce, M.C. Petty, A.J. Moore and Y.M. Lvov
Chemical Communications 14 (1990) 970-972.

13) *[†]A Rapid Method for the Evaluation of Small Catalyst Samples*
G.D. Moggridge, J.P.S. Badyal and R.M. Lambert
Journal of Vacuum Science and Technology A8 (1990) 3874-3875.

14) *[†]Surface Oxide Films and H_2/CO Chemisorption at the Ru/TiO_2 Interface: Studies with a Model Planar Catalyst*
J.P.S. Badyal and R.M. Lambert
J. Catalysis 130 (1991) 173-180.

15) *[†]Investigation of the SMSI Phenomenon with TiO_2/Ru/SiO_2 Model-Dispersed Catalysts*
J.P.S. Badyal, R.M. Lambert, K. Harrison, C. Riley and J. Frost
J. Catalysis 129 (1991) 486-496.

16) *Y-Ray Induced Fluoropolymeric Encapsulation of TiO_2 Particles: An XPS Investigation*
J.P.S. Badyal, Z. Chvatal, R.D. Chambers and R. Templeton-Knight
J. Chem. Soc. Faraday Transactions 87 (1991) 991-993.

17) *The Variation in Chemical Character of Plasma Polymerized Perfluorohexane*
A.G. Shard, H.S. Munro and J.P.S. Badyal
Polymer Communications 32 (1991) 152-154.

18) *[†]Investigation of the Strong Metal Support Interaction State of Ru/TiO_2 by ^{1}H Nuclear Magnetic Resonance.*
P. Jonsen, C.C.A. Riley, P. Meehan, J.C. Frost, K.J. Packer and J.P.S. Badyal
Catalysis Today 9 (1991) 121-127.

19) *[†]Highly-Conducting Langmuir-Blodgett Films Based on $Ni(dmit)_2$ Anions*
A.S. Dhindsa, J.P.S. Badyal, C. Pearson, M.R. Bryce and M.C. Petty.
Chemical Communications 5 (1991) 322-323.

20) *Plasma Versus UV Enhanced Oxidation of Polyethylene*
A.G. Shard and J.P.S. Badyal
Polymer Communications 32 (1991) 217-219.

21) *[†]An Electrical Investigation into Multilayer Assemblies of Charge-Transfer Materials*
J.J. Alekna, M. Petty, M.C. Petty, A.S. Dhindsa, J.P.S. Badyal and M.R. Bryce
Journal of Physics D: Applied Physics 24 (1991) 1422-1429.

22) *[†]Oxygen Surface Species on Lithium Nickelate Methane Coupling Catalysts and Their Interaction with Carbon Oxides*
G.D. Moggridge, J.P.S. Badyal and R.M. Lambert
J. Catalysis 132 (1991) 92-99.

23) *Plasma Oxidation Versus Photooxidation of Polystyrene*
A.G. Shard and J.P.S. Badyal
J. Physical Chemistry 95 (1991) 9436-9438.

24) *Surface Modification of PVDF by LiOH*
R. Crowe and J.P.S. Badyal
Chemical Communications 14 (1991) 958-959.

25) *Plasma Oxidation of Copper-Silver Alloy Surfaces*
J.M. Knight, R.K. Wells and J.P.S. Badyal
Chemistry of Materials 4 (1992) 640-641.

26) *Plasma Enhanced Chemical Vapour Deposition of Bulk Organosilicon Solids Using Hexamethyldisilane Precursor*
J.L.C. Fonseca, D.C. Apperley and J.P.S. Badyal
Chemistry of Materials 4 (1992) 1271-1275.

27) ***Surface Oxidation of Polyethylene, Polystyrene and PEEK: The Synthon Approach***
A.G. Shard and J.P.S. Badyal
Macromolecules 25 (1992) 2053-2054.

28) *Photooxidation of Polystyrene by O_2 and N_2O*
R.K. Wells and J.P.S. Badyal
J. Polymer Science, Polymer Chemistry Edn. 30 (1992) 2677-2681.

29) *Plasma Polymerization of Hexamethyldisilane onto Polyethylene Film*
J.L.C. Fonseca and J.P.S. Badyal
Macromolecules 25 (1992) 4730-4733.

30) †*Polyfluoroalkyl derivatives of polyethers*
J.P.S. Badyal, R.D. Chambers and A. Joel
J. Fluorine Chemistry 58 (1992) 334.

31) †*Electronic, Structural and Spectroscopic Properties of Langmuir-Blodgett Films of (O-Hexadecylthiocarboxy)tetrathiafulvalene (HDTTTF)*
A.S. Dhindsa, Y.-P. Song, J.P.S. Badyal, M.R. Bryce, Y.M. Lvov, M.C. Petty and J. Yarwood
Chemistry of Materials 4 (1992) 724-728.

32) †*Gamma-Ray Induced Encapsulation of Titanium Dioxide using Fluorinated Alkenes*
J.P.S. Badyal, R.D. Chambers, Z. Chvatal and G. Descelles
Journal of Fluorine Chemistry 57 (1992) 159-167.

33) ***Novel Surface Segregation Phenomena at the Plasma/Copper-Silver Alloy Interface***
J.M. Knight, J.L.C. Fonseca, Z.V. Hauptman and J.P.S. Badyal
Chemistry of Materials 5 (1993) 1221-1226.

34) *Plasma-Catalyzed Surface Rearrangement of Poly(ethylene) to a Poly(propylene) Type Structure*
R.K. Wells, I.W. Drummond, K.S. Robinson, F.J. Street and J.P.S. Badyal
Chemical Communications 6 (1993) 549-550.

35) *Photochemistry at the Organosilane / Polymer Interface*
R.K. Wells and J.P.S. Badyal
Macromolecules 26 (1993) 3187-3189.

36) *Plasma Polymerization of Tetramethylsilane*
J.L.C. Fonseca, D.C. Apperley and J.P.S. Badyal
Chemistry of Materials 5 (1993) 1676-1682.

37) *Modelling of Non-Isothermal Glow Discharge Modification of PTFE Using Low-Energy Ion Beams*
R.K. Wells, M.E.Ryan and J.P.S. Badyal
Journal of Physical Chemistry 97 (1993) 12879-12881.

38) *A Comparison of Plasma-Oxidized and Photo-Oxidized Polystyrene Surfaces*
R.K. Wells, I.W. Drummond, K.S. Robinson, F.J. Street and J.P.S. Badyal
Polymer 34 (1993) 3611-3613.

39) *Strong Metal-Support Interactions (Invited Review)*
J.P.S. Badyal
Chapter 10, in The Chemistry of Solid Surfaces and Heterogeneous Catalysis, Volume 6,

Elsevier, (1993) 311-340.

40) †*Partly Fluorinated Polyethers as Additives for Surface Modification*
J.P.S. Badyal, R.D. Chambers and A.K. Joel
J. Fluorine Chemistry 60 (1993) 297-300.

41) †*Catalysis in Ultra-High Vacuum: Oxidative Dehydrogenation of Cycloalkenes on Ag(111)*
S. Hawker, C. Mukoid, J.P.S. Badyal and R.M. Lambert
Vacuum 45 (1993) 275-278.

42) *Direct Evidence for the Generation of Phenyl Radicals and Cross-Linking During the Photolysis of Polystyrene Film*
R.K. Wells, A. Royston and J.P.S. Badyal
Macromolecules 27 (1994) 7465-7468.

43) *Surface Defluorination of PTFE by Sodium Atoms*
S. Tasker, R.D. Chambers and J.P.S. Badyal
Journal of Physical Chemistry 98 (1994) 12442-12446.

44) *Plasma Modification of Poly(ether sulfone)*
J. Hopkins and J.P.S. Badyal
Macromolecules 27 (1994) 5498-5503.

45) *Influence of Cross-Linking upon the Macroscopic Pore Structure of Cellulose*
S. Tasker and J.P.S. Badyal
Journal of Physical Chemistry 98 (1994) 7599-7601.

46) *A Comparative Study of the Silent Discharge Treatment of Saturated and Unsaturated Hydrocarbon Polymers*
O. D. Greenwood, S. Tasker and J.P.S. Badyal
J. Polymer Science, Polymer Chemistry Edn. 32 (1994) 2479-2486.

47) *Hydroxyl Accessibility in Celluloses*
S. Tasker, S.C.E. Backson, R.W. Richards and J.P.S. Badyal
Polymer 35 (1994) 4717-4721.

48) *Plasma-Enhanced Chemical Vapour Deposition of TiO_2/Polymer Composite Layers*
P.J. Ratcliffe, J. Hopkins, A.D. Fitzpatrick, C.P. Barker and J.P.S. Badyal
Journal of Materials Chemistry 4 (1994) 1055-1060.

49) *Plasma Oxidation of Polystyrene Versus Polyethylene*
R.K. Wells, I.W. Drummond, K.S. Robinson, F.J. Street and J.P.S. Badyal
Journal of Adhesion Science and Technology 7 (1993) 1129-1137.
Plasma Surface Modification of Polymers: Relevance to Adhesion, Editors M. Strobel, C.S. Lyons, and K.L. Mittal, 1994, VSP, ISBN 90-6764-164-2.

50) †*The Surface Modification of Polyethylene by Solution-Phase Photochemical Grafting Using Short Irradiation Times*
L.M. Hamilton, A. Green, S. Edge, J.P.S. Badyal, W.J. Feast and W.F. Pacynko.
Journal of Applied Polymer Science 52 (1994) 413-419.

51) *The Interfacial Chemistry of Metallized, Oxide Coated, and Nanocomposite Coated Polymer Films*
C.P. Barker, K.H. Kochem, K.M. Revell, R.S.A. Kelly and J.P.S. Badyal
Thin Solid Films 257 (1995) 77-82.

52) *Atmospheric Silent Discharge Versus Low-Pressure Plasma Treatment of Polyethylene, Polypropylene, Polyisobutylene, and Polystyrene*
O.D. Greenwood, R.D. Boyd, J. Hopkins and J.P.S. Badyal
Journal of Adhesion Science and Technology 9 (1995) 311-326.

53) *Plasma Polymerization of Sputtered Poly(tetrafluoroethylene)*
M.E. Ryan, J.L.C. Fonseca, S. Tasker and J.P.S. Badyal
Journal of Physical Chemistry 99 (1995) 7060-7064.

54) *Plasma Oxidation of Poly(cyclohexylmethylsilane) and Poly(phenylmethylsilane) Thin Films*
J.L.C. Fonseca, C.P. Barker and J.P.S. Badyal
Macromolecules 28 (1995) 6112-6115.

55) *AFM and Permeability Study of Stretching-Induced Gas Barrier Loss of AlO_x Layers*
C.P. Barker, K.H. Kochem, K.M. Revell, R.S.A. Kelly and J.P.S. Badyal
Thin Solid Films 259 (1995) 46-52.

56) *Surface Texturing of PTFE Film Using Non-Equilibrium Plasmas*
M.E. Ryan and J.P.S. Badyal
Macromolecules 28 (1995) 1377-1382.

57) ***Nonequilibrium Glow Discharge Fluorination of Polymer Surfaces***
J. Hopkins and J.P.S. Badyal
Journal of Physical Chemistry 99 (1995) 4261-4264.

58) †*Monolayer and Multilayer Films of Cyclodextrins Substituted with Two and Three Alkyl Chains*
M.H. Greenhall, P. Lukes, R. Kataky, N.E. Agbor, J.P.S. Badyal, J. Yarwood, D. Parker and M.C. Petty.
Langmuir 11 (1995) 3997 - 4000.

59) *Plasma Enhanced Chemical Vapour Deposition of Organosilicon Materials: A Comparison of Hexamethyldisilane and Tetramethylsilane Precursors*
J.L.C. Fonseca, S. Tasker, D.C. Apperley and J.P.S. Badyal
Macromolecules 29 (1996) 1705-1710.

60) *XPS and Atomic Force Microscopy of Plasma-Treated Polysulfone*
J. Hopkins and J.P.S. Badyal
Journal of Polymer Science: Part A: Polymer Chemistry Edn. 34 (1996) 1385-1393.

61) ***Plasma Fluorination Versus Oxygenation of Polypropylene***
J. Hopkins, R.D. Boyd and J.P.S. Badyal
Journal of Physical Chemistry 100 (1996) 6755-6759.

62) *Pulsed Plasma Polymerization of Perfluorocyclohexane*
A.M. Hynes, M.J. Shenton and J.P.S. Badyal
Macromolecules 29 (1996) 4220-4225.

63) ***Pulsed Plasma Polymerization of Maleic Anhydride***
M.E. Ryan, A.M. Hynes and J.P.S. Badyal
Chemistry of Materials 8 (1996) 37-42.

64) *Catalysis and Plasma Chemistry at Solid Surfaces*
J.P.S. Badyal
Topics in Catalysis 3 (1996) 255-264.

65) *Mechanistic Study of the Calcination of Supported Chromium(III) Precursors for Ethene Polymerization Catalysts*
V.J. Ruddick, P.W. Dyer, G. Bell, V.C. Gibson and J.P.S. Badyal
Journal of Physical Chemistry 100 (1996) 11062-11066.

66) *Plasma Polymerization of 2-Iodothiophene*
M.E. Ryan, A.M. Hynes, S.H. Wheale, C. Hardacre, R.M Ormerod and J.P.S. Badyal
Chemistry of Materials 8 (1996) 916-921.

67) *Plasma Polymerization of Trifluoromethyl-Substituted Perfluorocyclohexane Monomers*
A.M. Hynes, M.J. Shenton and J.P.S. Badyal
Macromolecules 29 (1996) 18-21.

68) *CF_4 Plasma Treatment of Asymmetric Polysulfone Membranes*
J. Hopkins and J.P.S. Badyal
Langmuir 12 (1996) 3666-3670.

69) *CF_4 Glow Discharge Modification of CH_4 Plasma Polymer Layers Deposited onto Asymmetric Polysulfone Gas Separation Membranes*
J. Hopkins and J.P.S. Badyal
Langmuir 12 (1996) 4205-4210.

70) [†]*Variation in Intermolecular Spacing with Dipping Pressure for Arachidic Acid LB Films*
S.A. Evenson, J.P.S. Badyal, C. Pearson and M.C. Petty.
Journal of Physical Chemistry 100 (1996) 11672-11674.

71) *Synergistic Oxidation at the Plasma / Polymer Interface*
J. Hopkins, S.H. Wheale and J.P.S. Badyal
Journal of Physical Chemistry 100 (1996) 14062-14066.

72) [†]*Skeletonization of Mixed Arachidic Acid / Cadmium Arachidate LB Films: A Study Using Atomic Force Microscopy*
S.A. Evenson, J.P.S. Badyal, C. Pearson and M.C. Petty.
Advanced Materials 9 (1997) 58 - 61

73) *CO Reduction of Calcined CrO_x / SiO_2 Ethene Polymerization Catalysts*
V.J. Ruddick and J.P.S. Badyal
Langmuir 13 (1997) 469 - 472

74) *AFM Study of the Breakup of Catalyst Particles During Ethylene Polymerization*
V.J. Ruddick and J.P.S. Badyal
Journal of Physical Chemistry B 101 (1997) 1791 - 1793

75) *Non-isothermal O_2 Plasma Treatment of Phenyl-Containing Polymers*
O.D. Greenwood, J. Hopkins and J.P.S. Badyal
Macromolecules 30 (1997) 1091-1098.

76) *Silent Discharge Treatment of Immiscible Polystyrene / Polycarbonate Polymer Blend Surfaces*
R.D. Boyd and J.P.S. Badyal
Macromolecules 30 (1997) 3658-3663

77) *Molecular Reaction Pathways During Plasma Modification of Polymer Surfaces*
J. Hopkins, R.D. Boyd and J.P.S. Badyal
Abstracts of Papers of the American Chemical Society, 213 (1997), POLY Pt2, 566.

78) [†]*An X-ray Absorption Spectroscopy Study of 2-Iodothiophene Plasma Polymers*
M.E. Ryan, A.M. Hynes, C. Hardacre, R.M Ormerod and J.P.S. Badyal
Synchrotron Radiation 2 (1997) 515-517.

79) *Plasma Chemistry at Polymer Surfaces (Invited Review)*
S. H. Wheale and J.P.S. Badyal
Chapter 10, in IUPAC Series *Chemistry for the 21st Century: Interfacial Science*, Blackwell Science (1997) 237 - 255.

80) *Adjacent Reentry of Folded Polydimethylsilane Polymer Chains*
R.D. Boyd and J.P.S. Badyal
Advanced Materials 9 (1997) 895 - 896.

81) *Nonequilibrium Plasma Treatment of Miscible Polystyrene/Poly(phenylene oxide) Blends*

R.D. Boyd and J.P.S. Badyal
Macromolecules 30 (1997) 5437-5442

82) *Atmospheric Nonequilibrium Plasma Treatment of Biaxially Oriented Polypropylene*
R.D. Boyd, A.M. Kenwright, D. Briggs and J.P.S. Badyal
Macromolecules 30 (1997) 5429-5436

83) *Self-Assembled PAMAM Dendrimer Films*
S.A. Evenson and J.P.S. Badyal
Advanced Materials 9 (1997) 1097 - 1099

84) ***Nonequilibrium Plasma Activation of Supported Cr(III) Phillips Catalyst Precursors***
V.J. Ruddick and J.P.S. Badyal
Journal of Physical Chemistry B 101 (1997) 9240 - 9243

85) *Early Stages of Ethylene Polymerization Using the Phillips CrO_x/Silica Catalyst*
V.J. Ruddick and J.P.S. Badyal
Journal of Physical Chemistry B, 102 (1998) 2991-2994

86) *Structure and Oxidative Plasma Degradation of Hexatriacontane Crystals*
R.D. Boyd, A.M. Kenwright and J.P.S. Badyal
Acta Polymerica 49 (1998) 129-132.

87) ***Non-Isothermal Plasma Metallization of Polymer-Supported Gold(III) Complexes***
J.M. Crowther and J.P.S. Badyal
Advanced Materials 10 (1998) 407 - 411.

88) *Selective Incorporation of Perfluorinated Phenyl Rings During Pulsed Plasma Polymerization of Perfluoroallylbenzene*
A. Hynes and J.P.S. Badyal
Chemistry of Materials 10 (1998) 2177-2182.

89) *Solventless attachment of long-chain molecules to poly(ethylene-alt-maleic anhydride) copolymer surfaces*
S.A. Evenson and J.P.S. Badyal
Journal of Physical Chemistry B 102 (1998) 5500-5502

90) *Chemical Reaction Pathways at the Plasma-Polymer Interface*
S.H. Wheale, C.P. Barker and J.P.S. Badyal
Langmuir 14 (1998) 6699-6704

91) *Atmospheric Versus Low Pressure Plasma Oxidation of Rubber Surfaces*
S.H. Wheale, J. Bech, N.H. Nilsson and J.P.S. Badyal
Polymer Surfaces and Interfaces III, Eds. R.W. Richards and S.K. Peace, Chapter 11, p285-297 (1999) J. Wiley & Sons Ltd.

92) *Plasmachemical Functionalization of Solid Surfaces with Low Surface Energy Perfluorocarbon Chains*
S.R. Coulson, I.S. Woodward, S.A. Brewer, C. Willis and J.P.S. Badyal
Langmuir 16 (2000) 6287-6293.

93) *Epoxide Functionalized Solid Surfaces*
C. Tarducci, E.J. Kinmond, S.A. Brewer, C. Willis and J.P.S. Badyal
Chemistry of Materials 12 (2000) 1884-1889.

94) ***Ultra-Low Surface Energy Plasma Polymer Films***
S.R. Coulson, I.S. Woodward, S.A. Brewer, C. Willis and J.P.S. Badyal
Chemistry of Materials 12 (2000) 2031-2038.

95) *Controlled Monomolecular Functionalization and Adhesion of Solid Surfaces*

S.A. Evenson, C.A. Fail and J.P.S. Badyal
Chemistry of Materials 12 (2000) 3038-3043.

96) *Super-Repellent Composite Fluoropolymer Surfaces*
S.R. Coulson, I.S. Woodward, S.A. Brewer, C. Willis and J.P.S. Badyal
Journal of Physical Chemistry B 104 (2000) 8836-8840.

97) ***Complexation of Fluorosurfactants to Functionalized Solid Surfaces: Smart Behaviour***
S. J. Hutton, J. M. Crowther and J.P.S. Badyal
Chemistry of Materials 12 (2000) 2282-2286.

98) *Switching Liquid Repellent Surfaces*
R. A. Lampitt, J. M. Crowther and J.P.S. Badyal
Journal of Physical Chemistry B 104 (2000) 10329-10331.

99) *Surface Esterification of Poly(ethylene-alt-Maleic Anhydride) Copolymer*
S.A. Evenson, C.A. Fail and J.P.S. Badyal
Journal of Physical Chemistry B 104 (2000) 10608-10611.

100) *Beyond the Surface (Feature Article)*
J.P.S. Badyal
Chemistry In Britain 37(1) (2001) 45-46.

101) *Plasmachemical Functionalization of Porous Polystyrene Beads*
S.P. Godfrey, E.J. Kinmond, I.R. Little and J.P.S. Badyal
Chemistry of Materials 13 (2001) 513-518.

102) *Surface Enrichment of Fluorochemical-Doped Polypropylene Films*
S.J. Ebbens and J.P.S. Badyal
Langmuir 17 (2001) 4050-4055.

103) *Cyano-Functionalized Solid Surfaces*
C. Tarducci, W.C.E. Schofield, S.A. Brewer, C. Willis and J.P.S. Badyal
Chemistry of Materials 13 (2001) 1800-1803.

104) ***Plasmachemical dehydroxylation of high surface area silica at room temperature***
S.P. Godfrey, I.R. Little and J.P.S. Badyal
Journal of Physical Chemistry B 105 (2001) 2572-2577.

105) *Surface Segregation and Plasma Oxidation of Poly(dimethylsiloxane)-Doped Polyolefins*
C.G. Spanos, S.J. Ebbens, A.J. Goodwin, P.J. Merlin and J.P.S. Badyal
Macromolecules 34 (2001) 8149-8155.

106) †*A Simple Method For The Quantitative Analysis of Resin Bound Thiol Groups*
J.P.S. Badyal, A.M. Cameron, N.R. Cameron, D.M. Coe, R. Cox, B.G. Davis, L.J. Oates, G. Oye and P.G. Steel
Tetrahedron Letters 42 (2001) 8531-8533.

107) *Controlled Attachment of PAMAM Dendrimers to Solid Surfaces*
C.A. Fail, S.A. Evenson, L.J. Ward, W.C.E. Schofield and J.P.S. Badyal
Langmuir 18 (2002) 264-268.

108) *Pulsed Plasma Deposition of Super-Hydrophobic Nanospheres*
D.O.H. Teare, C.G. Spanos, P. Ridley, E.J. Kinmond, V. Roucoules, S. Coulson, S.A. Brewer, C. Willis and J. P. S. Badyal
Chemistry of Materials 14 (2002) 4566-4571.

109) Synthesis of Cross-Linked Ethylene Glycol Dimethacrylate and Cyclic Methacrylic Anhydride Polymer Structures by Pulsed Plasma Deposition
C. Tarducci, W.C.E. Schofield, S.A. Brewer, C. Willis and J.P.S. Badyal

Macromolecules 35 (2002) 8724-8727.

110) Plasmachemical Amine Functionalization of Porous Polystyrene Beads: The Importance of Pore Architecture
G. Oye, V. Roucoules, A.M. Cameron, L.J. Oates, N.R. Cameron, P.G. Steel, B.G. Davis, D. Coe, R. Cox and J.P.S. Badyal
Langmuir 18 (2002) 8996-8999.

111) Monomolecular Functionalization of Pulsed Plasma Deposited Poly(2-hydroxyethyl methacrylate) Surfaces
C. Tarducci, W.C.E. Schofield, S.A. Brewer, C. Willis and J.P.S. Badyal
Chemistry of Materials 14 (2002) 2541-2545.

112) *Atmospheric Pressure Glow Discharge Deposition of Polysiloxane and SiOx Films*
L.J. Ward, W.C.E. Schofield, A.J. Goodwin, P.J. Merlin and J.P.S. Badyal
Langmuir 19 (2003) 2110-2114.

113) *Substrate-Independent Growth of Micropatterned Polymer Brushes*
D.O.H. Teare, W.C.E. Schofield, V. Roucoules and J.P.S. Badyal,
Langmuir 19 (2003) 2398-2403.

114) *Surface Segregation and Plasma Oxidation of Polyethylene-Poly(dimethylsiloxane) Copolymer Doped Polyethylene Films*
C.G. Spanos, S.J. Ebbens, A.J. Goodwin, P.J. Merlin and J.P.S. Badyal
Macromolecules 36 (2003) 368-372.

115) ***Atmospheric Pressure Plasma Deposition of Structurally Well-Defined Polyacrylic Acid Films***
L.J. Ward, W.C.E. Schofield, A.J. Goodwin, P.J. Merlin and J.P.S. Badyal
Chemistry of Materials 15 (2003) 1466-1469.

116) *Plasmachemical Amine Functionalization of Porous Polystyrene Spheres: The Importance of Particle Size*
G. Oye, V. Roucoules, A.M. Cameron, L.J. Oates, N.R. Cameron, P.G. Steel, B.G. Davis, D. Coe, R. Cox and J.P.S. Badyal
Journal of Physical Chemistry 1017 (2003) 3496-3499.

117) ***Super-Hydrophobic Surfaces Produced by Plasma Fluorination of Polybutadiene Films.***
I.S. Woodward, W.C.E. Schofield, V. Roucoules and J.P.S. Badyal,
Langmuir 19 (2003) 3432-3438.

118) †*Comparison of the effect of pore architecture and bead size on the extent of plasmachemical amine functionalisation of poly(styrene-co-divinylbenzene) permanently porous resins.*
J.P.S. Badyal, A.M. Cameron, N.R. Cameron, L.J. Oates, G. Oye, P.G. Steel, B.G. Davis, D. Coe and R. Cox
Polymer 45 (2004) 2185-2192

119) †*Plasmachemical Surface Functionalised Beads: Versatile Tailored Supports for Polymer Assisted Organic Synthesis*
J.P.S. Badyal, A.M. Cameron, N.R. Cameron, D. Coe, R. Cox, B.G. Davis, L.J. Oates, G. Oye, C. Spanos and P.G. Steel.
Chemical Communications (2004) 1402-1403.

120) *Diels-Alder Chemistry at Furan Ring Functionalized Solid Surfaces*
C. Tarducci, S.A. Brewer, C. Willis and J.P.S. Badyal
Chemical Communications (2005) 406-408.

121) *Diels-Alder Chemistry on Alkene Functionalized Films*
V. Roucoules, C.A. Fail, W.C.E. Schofield, D.O.H. Teare and J.P.S. Badyal
Langmuir 21 (2005) 1412 – 1415

122) *Solventless Coupling of Perfluoroalkylchlorosilanes to Atmospheric Plasma Activated Polymer Surfaces*
L.J. Ward, A.J. Goodwin, P.J. Merlin and J.P.S. Badyal
Polymer 46 (2005) 3986 – 3991

123) *High Structural Retention During Pulsed Plasma Polymerization of 1H,1H,2H-Perfluorododecene: an NMR and TOF-SIMS Study*
E.J. Kinmond, S.R. Coulson, S.A. Brewer, C. Willis and J.P.S. Badyal
Polymer 46 (2005) 6829-6835

124) ***Functionalization of Solid Surfaces with Thermoresponsive Protein-Resistant Films***
D.O.H. Teare, D.C. Barwick, W.C.E. Schofield, R.P. Garrod, A. Beeby and J.P.S. Badyal
Journal of Physical Chemistry B 109 (2005) 22407 – 22412

125) ***Pulsed Plasmachemical Deposition of Polymeric Salt Networks***
C.G. Spanos, A.J. Goodwin, P.J. Merlin and J.P.S. Badyal
Polymer 46 (2005) 8908-8912

126) *Rapid Polymer Brush Growth by TEMPO-Mediated Controlled Free-Radical Polymerization from Swollen Plasma Deposited Poly(maleic anhydride) Initiator Surfaces*
D.O.H. Teare, W.C.E. Schofield, R.P. Garrod and J.P.S. Badyal
Langmuir 21 (2005) 10818 – 10824

127) ***Poly(N-acryloylsarcosine methyl ester) Protein-Resistant Surfaces***
D.O.H. Teare, W.C.E. Schofield, R.P. Garrod and J.P.S. Badyal
Journal of Physical Chemistry B 109 (2005) 20923 – 20928

128) ***Substrate-Independent Approach for Polymer Brush Growth by Surface Atom Transfer Radical Polymerization***
D.O.H. Teare, D.C. Barwick, W.C.E. Schofield, R.P. Garrod, L.J. Ward and J.P.S. Badyal
Langmuir 21 (2005) 11425 – 11430

129) ***Re-Writable DNA Microarrays***
W.C.E. Schofield, J. McGettrick, T.J. Bradley, S. Przyborski and J.P.S. Badyal
Journal of the American Chemical Society 128 (2006) 2280-2285.

130) *Pulsed Plasma Polymerisation of Butylacrylate for Pressure-Sensitive Adhesion*
W.C.E. Schofield and J.P.S. Badyal
Plasma Chemistry and Plasma Processing 26 (2006) 361–369.

131) *Micropatterning of Plasma Fluorinated Super-Hydrophobic Surfaces*
I.S. Woodward, W.C.E. Schofield, V. Roucoules, T.J. Bradley and J.P.S. Badyal
Plasma Chemistry and Plasma Processing 26 (2006) 507–516.

132) *Electroless Metallization onto Pulsed Plasma Deposited Poly(4-vinylpyridine) Surfaces*
T. J. Bradley, W.C.E. Schofield, R.P. Garrod, and J.P.S. Badyal
Langmuir 22 (2006) 7552-7555.

133) *A Substrate-Independent Approach for Cyclodextrin Functionalized Surfaces*
W. C. E. Schofield, J. D. McGettrick, and J. P S. Badyal
Journal of Physical Chemistry B 110 (2006) 17161-17166.

134) ***Mimicking a Stenocara Beetle's Back for Microcondensation Using Plasmachemical Patterned Superhydrophobic-Superhydrophilic Surfaces***
R.P. Garrod, L.G. Harris, W.C.E. Schofield, J.D. McGettrick, L.J. Ward, D.O.H. Teare, and J.P.S. Badyal
Langmuir 23 (2007) 689-693.

135) ***Multi-Functional Molecular Scratchcards***

L.G. Harris, W.C.E. Schofield, and J.P.S. Badyal
Chemistry of Materials 19 (2007) 1546-1551.

136) *A Substrate-Independent Approach for the Surface Immobilization of Oligonucleotides Using Aldehyde Functionalized Surfaces*
J. D. McGettrick, W. C. E. Schofield, R. P. Garrod, and J. P. S. Badyal
Chemical Vapour Deposition 15 (2009) 122–127.

137) ***Rewritable Glycochips***
L. G. Harris, W. C. E. Schofield, K. J. Doores, B. G. Davis, and J. P. S. Badyal
Journal of the American Chemical Society 131 (2009) 7755–7761.

138) *Bromine Containing Functional Nanolayers for Biomolecule Immobilization*
J. D. McGettrick, T. Crockford, W. C. E. Schofield, and J. P. S. Badyal
Applied Surface Science 256S (2009) S30–S34.

139) *A Substrate-Independent Approach for Bactericidal Surfaces*
W. C. E. Schofield and J. P. S. Badyal
ACS Applied Materials and Interfaces 1 (2009) 2763–2767.

140) *Surface Actuation of Smart Nanoshutters*
S. Morsch, W. C. E. Schofield, and J. P. S. Badyal
Langmuir 26 (2010) 12342–12350.

8.2 Patents

J P S Badyal is the principal named inventor on all of the listed patents

141) *Porous Metal Composite Body*
T.R. Thomas and J.P.S. Badyal (Assigned to Mupor Ltd)
WO 95/25588 (28 September 1995)

142) *Surface Coatings*
J.P.S. Badyal, S.R. Coulson, C.R. Willis and S.A. Brewer
WO 98/58117 (23 December 1998)

143) *Metal deposition*
J.P.S. Badyal, J. Crowther and A.P. Gates
WO 99/08803 (25 February 1999)

144) *Applying fluoropolymer film to a body*
J.P.S. Badyal and S.J. Hutton
WO 99/32235 (1 July 1999)

145) *Epoxide Functionalised solid surfaces*
C. Willis, J.P.S. Badyal and S. Brewer
WO 00/78469 (28 December 2000)

146) *Surface treatment of an organic polymeric material*
A.J. Goodwin, D.E. Futter, P.J.J. Merlin and J.P.S. Badyal
WO 01/40359 (7 June 2001)

147) *Method and apparatus for forming a coating*
A. Goodwin, P. Merlin, J.P.S. Badyal and L. Ward
WO 02/28548 (11 April 2002)

148) *Surface Treatment*
A. Goodwin, P. Merlin, J.P.S. Badyal and L. Ward

WO 02/098962 (12 December 2002)

149) *Novel process for coating inhalation devices*
J.P.S. Badyal and P. Rogueda
WO 03/063938 (7 August 2003)

150) *Preparation of superabsorbent materials by plasma modification*
J.P.S. Badyal and W. Schofield
WO 03/080259 (2 October 2003)

151) *Method and apparatus for the formation of hydrophobic surfaces*
J.P.S. Badyal and I. Woodward
WO 03/080258 (2 October 2003)

152) *Protective coating composition*
A. Goodwin, J.P.S. Badyal, P. Merlin and C. Spanos
WO 03/084682 (16 October 2003)

153) *Apparatus for the coating and/or conditioning of substrates*
L. Ward and J.P.S. Badyal
WO 2005/021833 (10 March 2005)

154) *Fibrous products and methods of making and using them*
J.P.S. Badyal, L. Ward, D. York, A. Brooker, S. Summers J. Crowther, N. Roberts, A. Yates and S. Datta
WO 2005/028741 (31 March 2005)

155) *Method and apparatus for producing a coating on a substrate*
J.P.S. Badyal and L. Ward
WO 2006/092614 (8 September 2006)

156) *A method for producing a grafted polymer coating and substrates formed in accordance with the method*
J.P.S. Badyal, D. Teare and D. Barwick
WO 2006/097719 A1 (21 September 2006)

157) *A method for producing an aldehyde containing coating*
J.P.S. Badyal, W. Schofield and J. McGettrick
WO 2006/100480 (28 September 2006)

158) *Thiol functionalised coatings and method for producing the same*
J.P.S. Badyal and W. Schofield
WO 2006/109014 (19 October 2006)

159) *Method for producing, and a substrate with, a surface with specific characteristics*
J.P.S. Badyal, D. Teare and W. Schofield
WO 2006/109055 (19 October 2006)

160) *A method for producing a nitrogen functionalised surface*
J.P.S. Badyal, D. Teare and W. Schofield
WO2006111711, 24th October 2006.

161) *An article, and a method for creating the article, with a chemically patterned surface*
J.P.S. Badyal, J. McGettrick and L. Harris
WO 2006/117527 (9 November 2006)

162) *Method of Coating Medical Devices*
J.P.S. Badyal and A. Broad
EP No 06254456.4, 25th August 2006

163) *Deposition of Anhydride Layers*
T. Wood, W.C.E. Schofield, and J.P.S. Badyal
GB Pat. Appl. No. 1006886.4, 24th April 2010.

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ANNEX II

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Declarant's signature:

Jas Pal Singh Badyal

Jas Pal Singh BADYAL

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PLASMA POLYMERIZATION OF ETHYLENE IN AN ATMOSPHERIC PRESSURE DISCHARGE

Kevin G. Donohoe and Theodore Wydeven
Ames Research Center, NASA, Moffett Field, California 94035

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ABSTRACT

The polymerization of ethylene in an atmospheric pressure pulsed discharge has been studied. Partial pressures of ethylene up to 4 kN/m^2 were used with helium as a diluent. Deposition rates were the same throughout the discharge and were in the 1-2 Å/sec range. The films were clear, soft, and adhered well to glass substrates. Oligomers that scattered 637.8-nm light were always observed in the gas phase. The results suggest that Brownian diffusion of these oligomers was the rate limiting step in film deposition.

1. INTRODUCTION

At present, most reported plasma processes are carried out at low pressures, usually 300 N/m^2 or less. We describe here a plasma polymerization reactor which operates at atmospheric pressure (101 kN/m^2). The interest in operating at this pressure is based on its potential economic advantages. Also, it was anticipated that operation at high partial pressure of monomer might result in high film deposition rates. Ethylene monomer was chosen because its polymerization has been studied in detail in low pressure discharges.[1,2]

2. EXPERIMENTAL

Discharge Circuit. The circuit and reactor are shown in Fig. 1. The circuit consists of a high voltage 60-Hz power supply which charges the capacitor C in an LC resonant circuit to a voltage determined by the spark gap electrode separation. When the spark gap fires, the circuit resonates with a frequency near $1/\sqrt{LC}$. This excites the secondary of the Tesla transformer and a large ac voltage is applied across the electrodes in the reactor. The rate at which the spark gap fires is controlled by the setting of the variable transformer.

Breakdown waveforms are shown in Fig. 2. Since the circuit and the electrodes are symmetric, the breakdown waveforms do not depend on the initial polarity. The breakdown waveforms show two characteristics: a breakdown voltage, V_b, and an extinction voltage, V_e. V_b is the voltage at which the circuit begins to load down due to current flow through the plasma and V_e is the voltage at which current stops flowing. The current is a pulse which begins at V_b, reaches a maximum, and drops to zero at V_e; it flows

for about 100 ns. So, at a spark gap firing rate of 480/sec, a discharge occurs 480 times per second.

The reactor (Fig. 1) consists of a glass pipe cross with a 15.2 cm i.d. in the direction of gas flow and a 10.6 cm i.d. along the electrode axis. The electrodes, which were brass disks 9.5 cm in diameter and 1.25 cm thick with edges of 0.16-cm radii, were potted in polyester casting resin and machined to 11.43-cm diameter with a 0.318-cm-thick polyester coating on each electrode face. This design permits the production of a uniform discharge by limiting but not preventing secondary cathode emission.[3] Secondary emission still occurred at the joint between the resin and the 0.95-cm-diameter stem at the back of each electrode. An electrode gap of 3.81 cm was used.

3. RESULTS

Operation of a uniform glow discharge in pure ethylene was not possible at atmospheric pressure. A discharge in pure ethylene constricted at pressures above 4 kN/m^2. With helium as a diluent, a uniform discharge could be maintained at a partial pressure of ethylene of 8 kN/m^2. This increase in the maximum partial pressure of ethylene is due in part to the high thermal conductivity of helium and to the fact that constriction under these conditions is thermal in nature.[3,4]

Films were deposited on glass microscope slides oriented parallel to the electrode faces. Deposition rates were independent of vertical position and were the same on the lower and upper surfaces of the glass slides. Unless otherwise noted, all of the results discussed below relate to films which were of uniform thickness.

In all cases, the plasma polymerized ethylene films were uncolored, soluble in ethanol, and had an olefinic odor (similar to ethylene) which disappeared after a few weeks of storage in room air.

Infrared transmission spectra of films deposited on cesium iodide windows showed no absorption around 1600 cm^{-1}, indicating the absence of significant amounts of vinyl groups or unsaturation in the polymer films.

Elemental analysis of a typical film yielded the following empirical formula: $C_2H_{3.26}O_{0.23}$. Typical literature values[5] for n in C_2H_n are in the range of 2.6-3 for rf discharge-produced ethylene films, while for linear conventional polyethylene, $n = 4$. The lower degree of hydrogen abstraction observed here ($n = 3.26$) suggests that less unsaturation or crosslinking is present in the polymer films produced here at atmospheric pressure than at low pressure in an rf discharge.

An important difference between polymerization in this atmospheric pressure pulsed discharge and in low pressure rf discharges is that in the high pressure discharge, oligomers large enough to visibly scatter light from a He-Ne laser (632.8 nm) were always observed in the gas phase. Under conditions in which uniform clear films were produced, these scattering centers were uniformly distributed throughout the discharge volume. Qualitatively, their gas phase density (estimated visually under laser light illumination) was highest under conditions of highest rates of deposition (up to 3 Å/sec). However, the films produced at these high rates were not clear; they were fogged and almost opaque. It has been noted that in low pressure discharges, high deposition rates are also accompanied by powder formation and the production of opaque films.[6] Fogging

of films can be caused by surface roughness or by the presence of scattering centers embedded in the bulk film. A prior scanning electron microscope (SEM) study of particle incorporation in plasma polymerized organosilicon films[7] showed that submicrometer diameter spheres were uniformly distributed throughout the polymer films. No such particles were observed with the films produced here (25-nm resolution). Thus, the fogged appearance of these films was apparently caused by surface roughness, and not by the presence of particles embedded in the film.

The magnitude of the surface roughness required to cause fogging can be estimated. Diffuse reflectance begins when the roughness height h is greater than $\lambda/16$ for normal incidence of light of wavelength λ.[8] For visible light (400-700 nm), this corresponds to h between 25 and 44 nm. SEM examination of a fogged film surface revealed the presence of surface roughness on the film surface (Fig. 3). This SEM photograph was taken with the sample at an angle of 45° relative to the electron beam. Particles with 800 to 5000 nm (0.8-5 μm) diameters are evident in the figure, and they appear to protrude from the surface by 400-2500 nm. It is evident from Fig. 3 that the larger particles are agglomerates of smaller ones. SEM examination of a clear film showed absolutely no structure (25-nm resolution). So, under conditions in which clear films are deposited, the gas phase oligomers could be either too small to produce diffuse reflectance on the surface (smaller than 25 nm) or they could incorporate homogeneously into the bulk polymer film.

Effect of Spark Gap Firing Rate. The power in a pulsed discharge can be varied either by the power per pulse or by the pulse repetition rate. With the circuit used here, the power per pulse can be varied by the magnitude of the spark gap electrode separation. The spark gap firing rate can be varied by changing the output of the variable transformer (Fig. 1). Because the voltages and current did not vary with the firing rate (from 60-840/sec), the average power varied directly with the firing rate. This power was 0.5 W at a rate of 480/sec with a peak pulse power of 15 kW.

The effect of varying the firing rate is shown in Fig. 4. The film deposition rate varies linearly with the firing rate up to a rate of 600/sec, suggesting that a constant amount of polymer is formed each time a discharge occurred. For rates greater than 600/sec, the deposition rate increased nonlinearly, indicating that some change in the mechanism(s) of deposition occurred, or that a nonlinear relationship between the production of active species and the firing rate existed. The low average power of 1 W at 600/sec suggests that temperature changes were not responsible for the nonlinear relationship between firing rate and deposition rate.

The ethylene concentration was also measured. A sampling probe and gas chromatograph were used to sample ethylene inside the discharge. Ethylene concentrations were constant in the direction parallel to the electric field and decreased nearly linearly in the flow direction. Therefore, concentrations were measured in the center of the discharge. Figure 4 shows that the extent of reaction $(c_o-c)/c_o$ was proportional to the firing rate even at the high rates for which the deposition rate was not proportional to the firing rate. Here, c is the measured ethylene concentration and c_o is the feed concentration. The linearity of the extent of reaction curve in Fig. 4 and the nonlinearity of the deposition rate curve in the same figure demonstrate that the deposition rate did not vary directly with the amount of ethylene consumed.

Effect of Gas Flow Rate. Figure 5 shows the film deposition rate vs. the flow rate of feed for two feed concentrations. The range of flows corresponds to mean residence times from 60 sec to 1290 sec (the flow rates are at NPT). The characteristic time for diffusion of ethylene across the discharge zone is 7 sec. Hence, the reactor was operated at flow rates for which diffusion was fast compared to convection. In Fig. 5, the deposition rate is seen to be virtually independent of flow rate for flows greater than 5 cm^3/sec. Below 5 cm^3/sec the rate increases to a maximum and then decreases. At the low flow rates, the deposition rate is limited by the supply of monomer. As the flow rate is increased, a point is reached at which the gas residence time becomes insufficient for large gas phase free radical concentrations to be attained and consequently the deposition rate declines as the flow rate is further increased. The plateau in deposition rate suggests that at high monomer flow rates deposition is controlled not by gas phase processes but rather by processes occurring at the plasma-substrate interface. Thus, the free radicals necessary for polymer formation might be formed via the impact of ions and electrons with the growing polymer film. It is likely that deposition is controlled by radical formation both at the surface and in the gas phase for low monomer flow rates and at the surface alone for high monomer flow rates.

Gaseous Discharge Products. Gas chromatographic analyses of the gas in the discharge showed that acetylene was the major volatile product. Ethane was also produced but in a much lower concentration than acetylene: the ratio of ethane to acetylene concentration was typically in the 0.02-0.07 range. No other gaseous products were observed (within the detection limits of the chromatograph). These results are similar to those obtained by others[5] in a mass spectrometric analysis of the effluent from a low pressure rf discharge in ethylene.

4. DISCUSSION

The most obvious difference between films that were produced under different conditions in this work was their surface morphology. Because light-scattering oligomers were always observed in the gas phase when film deposition occurred, it is likely that the observed micrometer-sized particles in the fogged film surfaces were individual oligomers or aggregates of oligomers. The difference between the oligomers which form when fogged or clear films were deposited is likely to have been the size to which they grow in the gas phase before reaching the growing film surface. It is also possible that they differed chemically and that the oligomers present under conditions in which fogged films were formed were not reactive enough to form a smooth surface. In both cases, the oligomers may have been oils or polyradicals.

The following discussion includes a description of the motion of these oligomers in the gas phase and a description of the proposed gas phase chemical reactions.

Chemical Reactions in the Gas Phase. Chromatographic analysis of the gas in the discharge showed that the rate of disappearance of ethylene did not vary directly with the film deposition rate. It also revealed that acetylene was the principal gaseous product of the ethylene-helium discharge and only traces of higher molecular weight hydrocarbons were present. The

appearance of acetylene is consistent with a free radical mechanism for polymerization similar to the one proposed[5] to describe the low pressure polymerization of ethylene in an rf discharge. In this mechanism, initiation is by electron impact on C_2H_4, propagation is by radical addition to C_2H_4, and termination occurs by the reaction between two radicals.

Oligomer Motion in the Gas Phase. The observation that the film deposition rate was nearly independent of feed concentration, flow rate, and extent of ethylene reaction over wide ranges of these variables, suggested that some mass transfer process limited the deposition rate. Therefore, an attempt was made to relate the motion of the oligomers in the gas phase to the observed deposition rates.

The motion of micrometer- and submicrometer-sized particles in the gas phase can be due to convection, Brownian motion, and sedimentation. Convection occurred perpendicular to the direction of the mass flux that produces deposition and was considered unimportant under conditions of uniform deposition. In helium at NPT, the Brownian displacement of a particle in 1 sec equals the sedimentation displacement for particles of the order of 500-nm diameter and unit density.[9] For particles smaller than 500-nm diameter, Brownian motion dominates sedimentation. This can explain why the deposition rate of clear films was observed to be the same on the top and bottom of glass cover slips positioned between the electrodes.

It is of interest to note that limited agglomeration of the oligomers would have a relatively small effect on the Brownian motion of the agglomerates because the Brownian diffusion coefficient varies with the reciprocal of the particle radius. For example, a twofold increase in the particle radius requires an eightfold increase in its mass. This means that eight particles would have to combine to decrease the Brownian diffusion rate by a factor of 2. This relatively insensitive response of the diffusion coefficient to agglomeration is a likely explanation for the fact that the deposition rate is independent of gas flow rate over such a large range of flow rates.

5. SUMMARY AND CONCLUSIONS

Plasma polymerization of ethylene has been studied in a pulsed electrical discharge which operated at atmospheric pressure. Films produced in this discharge were soft, uncolored, soluble in ethanol, and passed the cellophane tape pull test for adhesion to a glass substrate. These observations, coupled with the infrared spectra and elemental analysis of the polymer, indicated that the degree of unsaturation and/or crosslinking was low. The low degree of hydrogen abstraction and lack of crosslinking is consistent with the low average electron energies (due to the low electric field-to-pressure ratio) present in the high pressure discharge.

A free radical chain reaction scheme[5] to explain the polymerization is consistent with the results obtained in this work. Gas chromatographic analysis of the gas in the plasma revealed that acetylene was the principal gaseous product of the ethylene-helium discharge and only traces of higher molecular weight hydrocarbons were present. Brownian diffusion of the oligomers formed in the gas phase is suggested to be the rate-limiting step in the film deposition process under the conditions of constant firing rate and low duty cycle.

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REFERENCES

(1) H. Kobayashi, A. T. Bell, and M. Shen, J. Appl. Polym. Sci., 17, 885 (1973).

(2) A. T. Bell, T. Wydeven, and C. Johnson, J. Appl. Polym. Sci., 19, 1911 (1975).

(3) K. G. Donohoe and T. Wydeven, J. Appl. Polym. Sci., 1979.

(4) W. H. Bennett, Phys. Rev., 45, 890 (1934).

(5) H. Kobayashi, M. Shen, and A. T. Bell, J. Macromol. Sci. Chem., A8(2), 373 (1974).

(6) H. Kobayashi, M. Shen, and A. T. Bell, Macromolecules, 7(3), 277 (1974).

(7) L. F. Thompson and G. Smolinsky, J. Appl. Polym. Sci., 16, 1179 (1972).

(8) P. Beckmann and A. Spizzichino, "The Scattering of Electromagnetic Waves from Rough Surfaces" (Macmillan Co., New York, 1973).

(9) R. D. Cadle, "Particle Size" (Reinhold, New York, 1965, Ch. 2).

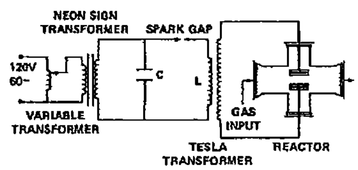

Fig. 1. Schematic of the discharge circuit and reactor.

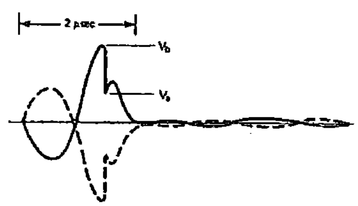

Fig. 2. Oscillogram of the breakdown voltage waveforms.

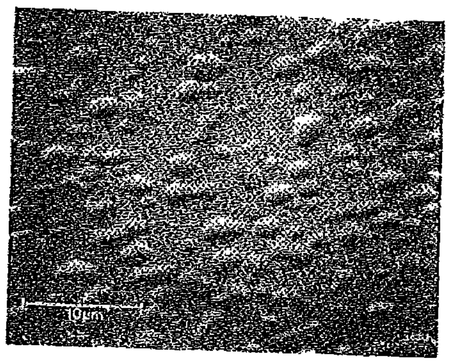

Fig. 3. SEM photograph of a fogged film with the sample at an angle of 45° relative to the electron beam.

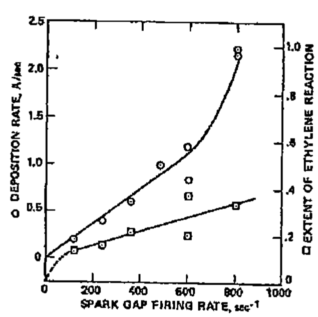

Fig. 4. Film deposition rate (O) and extent of ethylene reaction (□) vs. spark gap firing rate.

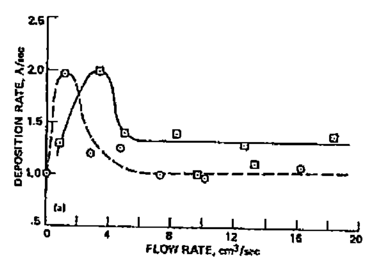

Fig. 5. Film deposition rate vs. gas flow rate (NPT). O – 1% C_2H_4 in feed, □ – 2% C_2H_4 in feed. Firing rate: 480 s^{-1}.